

# **Determination of Desorbed Species During Heating of Agl-Mordenite, Provided by ORNL**

## **Fuel Cycle Research & Development**

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Materials Recovery and Waste Form Development

*Prepared for*  
*U.S. Department of Energy*  
*Office of Nuclear Energy –*  
*Separations Working Group*  
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*December 15, 2015*  
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## SUMMARY

This study is focused on describing the desorbed off gases due to heating of the AgI-Mordenite (MOR) produced at ORNL for iodine ( $I_2$ ) gas capture from nuclear fuel aqueous reprocessing. In particular, the interest is for the incorporation of the AgI-MOR into a waste form, which might be the Sandia developed, low temperature sintering, Bi-Si oxide based, Glass Composite Material (GCM). The GCM has been developed as a waste form for the incorporation any oxide based getter material. In the case where iodine may be released during the sintering process of the GCM, additional Ag flake is added as further insurance in total iodine capture and retention. This has been the case for the incorporated ORNL developed AgI-MOR.

Thermal analysis studies were carried out to determine off gasing processes of ORNL AgI-MOR. Independent of sample size, ~7wt% of total water is desorbed by 225°C. This includes both bulk surface and occluded water, and are monitored as  $H_2O$  and  $OH$ . Of that total, ~5.5wt% is surface water which is removed by 125°C, and 1.5wt% is occluded (in zeolite pore) water. Less than ~1 wt% total water continues to desorb, but is completely removed by 500°C.

Above 300°C, the detectable remaining desorbing species observed are iodine containing compounds, including  $I$  and  $I_2$ .

## ACKNOWLEDGEMENTS

The authors thank S. Bruffey and R. Jubin (ORNL) for AgI-Mordenite sample. We acknowledge funding from the DOE/NE Fuel Cycle R&D – Materials Recovery and Waste Form Development (MRWFD).

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## 1. ABBREVIATIONS AND ACRONYMS

Ag	Silver
Ag <sup>o</sup>	Silver metal
AgI	Silver Iodine
Bi	Bismuth
°C	Degrees Celsius
DSC	Differential Scanning Calorimetry
FCRD	Fuel Cycle Research and Development
FY	Fiscal Year
g	Gram
GCM	Glass Composite Materials (waste form)
hr	Hour
I	Iodine
I <sub>2</sub>	Iodine (gas)
L	Liter
min	Minute
MOR	Mordenite Zeolite
MS	Mass Spectroscopy
ORNL	Oak Ridge National Laboratory
SNL	Sandia National Laboratories
TGA	Thermo Gravimetric Analysis
XRD	X-ray Diffraction

## 2. INTRODUCTION

In the spent nuclear fuel reprocessing procedures under consideration by the US Department of Energy, off-gas containing  $^{129}\text{I}_2$  and organic- $^{129}\text{I}$  vapors is passed through a bed of a silver-exchanged  $\text{Ag}^\circ$ -Mordenite ( $\text{Ag}^\circ$ -MOR), that selectively captures the  $^{129}\text{I}$  to form  $\text{AgI}$ -MOR.<sup>1,2</sup> The majority of the captured  $^{129}\text{I}$  reacts with the silver in the  $\text{Ag}^\circ$ -MOR to form  $\text{AgI}$ , while the rest is either chemically adsorbed, or passed downstream. Silver iodide (melting point =  $558^\circ\text{C}$  and density =  $5.675\text{ g/cm}^3$ )<sup>3</sup> has a low solubility in water,  $3 \times 10^{-6}\text{ g/L}$  at  $20^\circ\text{C}$ <sup>3</sup> (corresponding to a  $K_{\text{sp}}$  of  $10^{-16.1}$ ), which makes silver a good candidate for the capture of  $^{129}\text{I}$ . For safe storage, the  $\text{AgI}$ -MOR must be incorporated into a dense, durable solid waste form, so that the release of  $^{129}\text{I}$  is inhibited with time or environmental contact. Because of their flexibility of synthesis and chemical durability, low temperature sintering glasses are being examined for the encapsulation of  $\text{AgI}$ -MOR iodine capture materials to form Glass Composite Materials (GCMs), for subsequent use as waste forms.<sup>4-7</sup> They are easier and less expensive to prepare than conventional ceramics but also offer high durability, as shown in our recent work.<sup>8</sup>

In our previous reports<sup>5-8</sup> on  $\text{I}_2$ -loaded  $\text{Ag}^\circ$ -MOR, we identified a commercially available low-temperature sintering glass powder based on silicon and bismuth oxides that sinters to full density at  $550^\circ\text{C}$  and has excellent durability. To prevent surface/bulk chemisorbed  $\text{I}_2$  vapor from escaping from the zeolite during GCM sintering, additional Ag flake was added to the GCM mixture to capture the desorbing  $\text{I}_2$  vapor. As a note, little to no Ag flake is necessary if the GCM is sintered in inert atmosphere,<sup>9</sup> an option for future scaleup studies.

This study is focused on describing the desorbed off gases due to heating of the  $\text{AgI}$ -Mordenite (MOR) produced at ORNL for iodine ( $\text{I}_2$ ) gas capture from nuclear fuel aqueous reprocessing. In particular, the interest is for the incorporation of the  $\text{AgI}$ -MOR into a waste form, which might be a Sandia developed, low temperature sintering, Bi-Si oxide based, Glass Composite Material (GCM). The GCM has been developed as a waste form for the incorporation any oxide based getter material. In the case where iodine may be released during the sintering process of the GCM, additional Ag flake is added as further insurance in total iodine capture and retention. This has been the case for the ORNL developed  $\text{AgI}$ -MOR. To study what species are evolving off the  $\text{AgI}$ -MOR with heating, we undertook an extensive thermal analysis study with a sample provided by ORNL.



### 3. EXPERIMENTAL METHODS

#### 3.1 Starting Materials

AgI-MOR was provided by ORNL. It was labeled a “I<sub>2</sub>-loaded Mordenite “AgZ-I” (SHB)”, and sent with the description: “Mordenite was exposed to dry air stream containing 50ppm I<sub>2</sub> for 5 days, then purged with dry air for 2 days to remove any physisorbed iodine.”

#### 3.2 Characterization Methods

Simultaneous thermogravimetric analysis and differential scanning calorimetry (TGA/DSC, SDTQ600, TA Instruments, Newcastle, DE) with mass spectroscopic (MS, Thermo Star<sup>TM</sup>, Pfeiffer Vacuum, Inc., Asslar, Germany) off-gas analysis was performed on powder samples of the as-received AgI-aerogel materials, the powdered as-received aerogel materials, and the mixed AgI-aerogel with added Ag flake. Heating experiments were performed in air at 5°C/min heating rate, and a 300ml/min flow rate of air. Samples were also studied by powder X-ray diffraction (XRD, Siemens Kristalloflex D 500 diffractometer, Bruker-AXS Inc., Madison, WI).

#### 3.3 AgI-MOR Characterization

Powder X-ray Diffraction (XRD): The pattern has standard broad peak diffraction patterns of MOR (natural) plus the sharp peaks of AgI. See figure 1. The large sharp peaks indicate large quantities of surface (not in-pore) AgI.

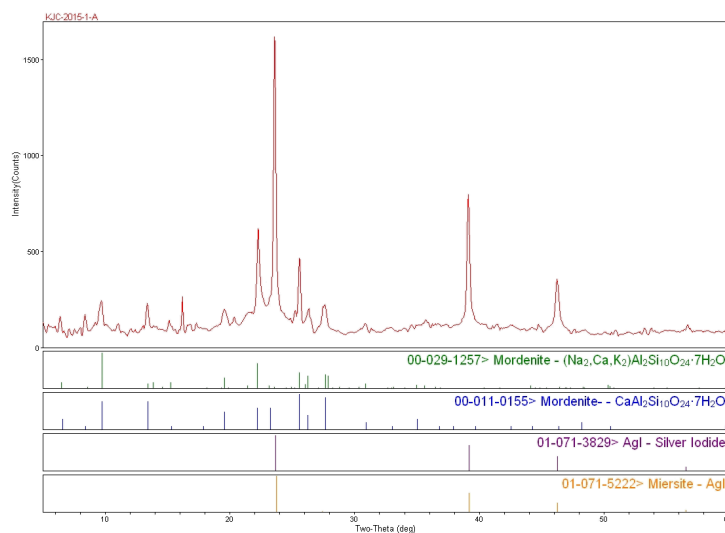


Figure 1: XRD of ORNL AgI-MOR with JCPDS library matches.

### 3.4 Thermal Characterization of AgI-MOR

TGA/MS: Thermal analysis studies were carried out to determine off gasing processes of ORNL AgI-MOR. Two different sample sizes of the same ORNL material were studied, 30.396mg (figure 2) and 15.182mg (figure 3). They were run in air at a flow rate of 300ml/min.

Independent of sample size, ~7wt% of total water is desorbed by 225°C. This includes both bulk surface and occluded water, and are monitored as H<sub>2</sub>O and OH. Of that total, ~5.5wt% is surface water which is removed by 125°C, and 1.5wt% is occluded (in zeolite pore) water. Less than ~1 wt% total water continues to desorb, but is completely removed by 500°C.

Above 300°C, the detectable remaining desorbing species observed are iodine containing compounds, including I and I<sub>2</sub>.

Independent of sample size (no effect of diffusion pathlength for offgas detection), the weight loss, temperatures, and off gas identification by mass spec were consistent between the two samples (see figures 2-4).

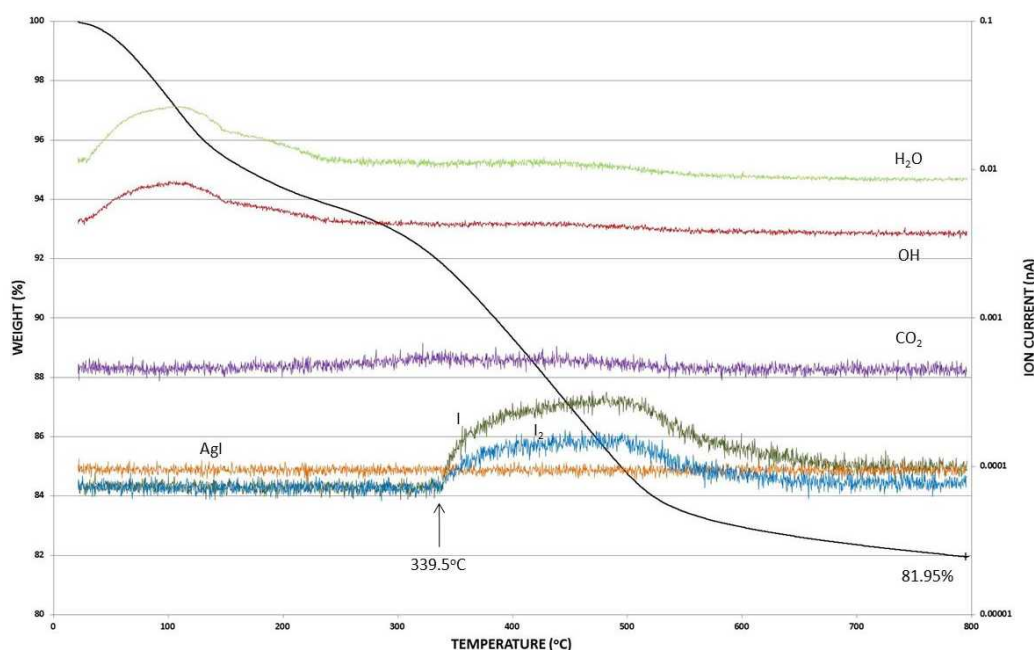


Figure 2: TGA/MS of ORNL sample, “I<sub>2</sub>-loaded Mordenite AgZ-I SHB 2/9/15”.  
Purge gas: Air; Purge Rate: 300 ml/min; sample size: 30.396mg.

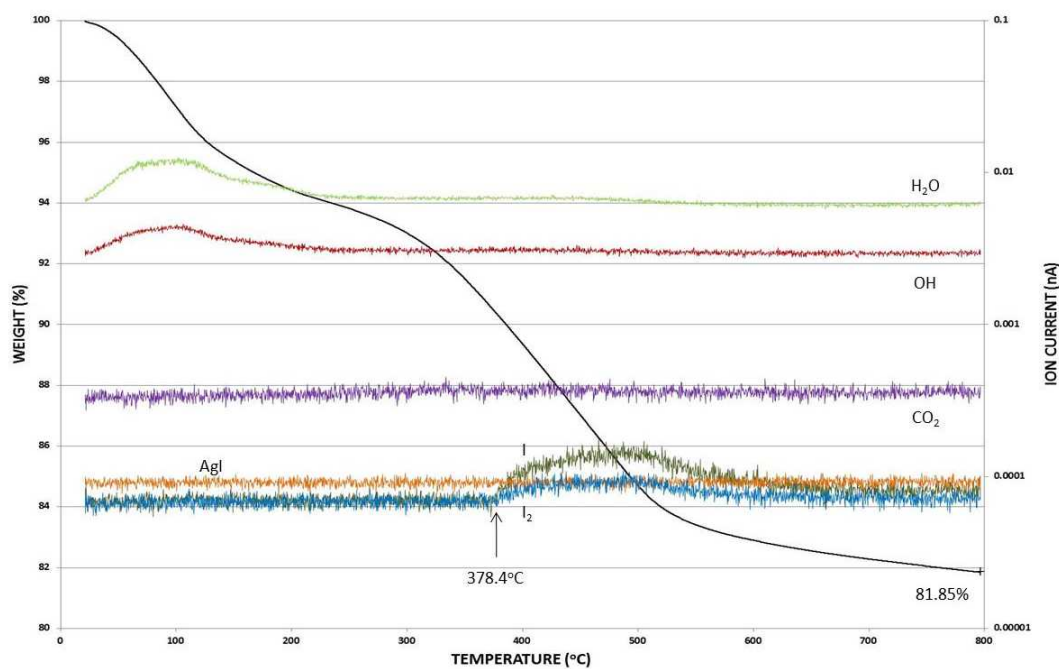


Figure 3: TGA/MS of ORNL sample, “ $I_2$ -loaded Mordenite AgZ-I SHB 2/9/15”.  
Purge gas: Air; Purge Rate: 300 ml/min; sample size: 15.182 mg.

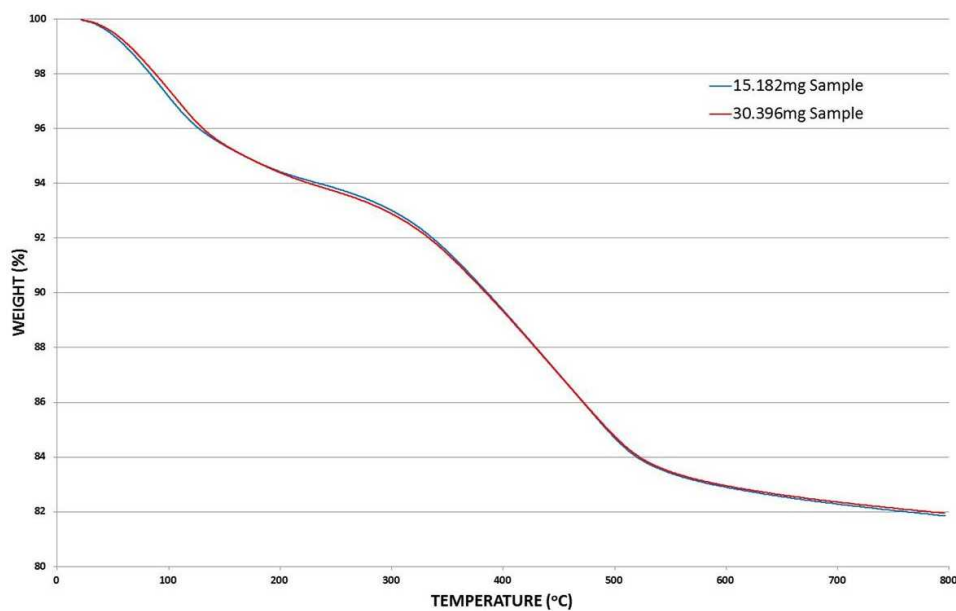


Figure 4: TGA curves (overlay) of both 30.396mg and 15.182mg samples.  
“ $I_2$ -loaded Mordenite AgZ-I SHB 2/9/15”.  
Purge gas: Air; Purge Rate: 300 ml/min

## 4. CONCLUSIONS

Thermal analysis studies were carried out to determine off gasing processes of ORNL AgI-MOR. Independent of sample size, ~7wt% of total water is desorbed by 225°C. This includes both bulk surface and occluded water, and are monitored as H<sub>2</sub>O and OH. Of that total, ~5.5wt% is surface water which is removed by 125°C, and 1.5wt% is occluded (in zeolite pore) water. Less than ~1 wt% total water continues to desorb, but is completely removed by 500°C.

Above 300°C, the detectable remaining desorbing species observed are iodine containing compounds, including I and I<sub>2</sub>.

We believe that incorporation of the ORNL AgI-MOR in the GCM, with silver flake added to capture volatilized iodine to form AgI, will result in a durable waste form on par with that recorded with AgI-MOR incorporation into the GCMs.<sup>8</sup> Furthermore, past studies of ours shown that the iodine is better entrapped in the Ag-MOR when a number of other variables are introduced to the zeolite Mordentie for iodine capture. These include: (1) use of a non-natural/geologic MOR (which is much more highly crystalline and does not contain many competing cations), (2) Ag-MOR that is purely synthesized (such as UOP LZM-5), (3) is more completely ion exchanged so that the only charge balancing cation is silver, (4) use of a nonreduced Ag-MOR, (5) improved resonance time for iodine gas and sorbent, and (5) use of an Ag-MOR that is not pelletized or that might contain a binder that that does not significantly reduce the surface area and access to the zeolite pores, as is the case with the current ORNL Ag-MOR.

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## 6. APPENDIX A

This is additional information about the TGA-MS system used for this study; in particular it discusses how the instrument settings can affect the results. The mass spectrometer used is connected to the TGA by a capillary. The software running the TGA and MS are unique and the software programs do not communicate; the TGA software has no control over the MS software and cannot read or change any MS settings during the measurement. The MS data is simply converted to a format after the measurement that the TGA software can read and match to the TGA data.

The MS uses a high speed turbo pump to create suction on the capillary connecting the two instruments; the other end is inserted into the TGA exhaust vent to capture a small portion of the gases generated from the sample near the sample pan. Plus, it draws in some of the TGA purge gas. The turbo pump does not change speed at any time during the measurements and maintains a nearly constant vacuum on the capillary; this can create the illusion of changes in the amounts of the off-gas products of water and carbon dioxide that are not reflected in the TGA results.

As the temperature of the TGA furnace increases, the purge gas entering the furnace rapidly heats to the current temperature. Because the exhaust vents to the atmosphere, the pressure inside the furnace will not change. The amount of purge gas entering the furnace ( $n$ ) does not change;  $R$  is constant and the pressure is constant. Based on the ideal gas law,  $PV=nRT$ , as the temperature increases, the volume increases – forcing increased volume to exit the exhaust vent. As the temperature increases, more gas molecules exit the furnace exhaust. This results in decreased molecule count for the MS to draw into the capillary. Since the MS turbo speed does not change, the MS continues to attempt to draw in the same amount of gas molecules, regardless of furnace temperature. Room air is drawn in around the end of the capillary at the attachment to the furnace; this joint is snug but is NOT a tight seal and is not meant to be. As the furnace temperature continues to increase, room air continues to make up a larger portion of the gases drawn into the MS; so the MS signals obtained for water continue to increase, even though the sample may not be releasing any additional water.

Figure A1 displays this phenomenon using an empty, dry sample pan. The only gases being drawn into the MS are those of the ambient air and purge gas (dry air cylinder of oxygen (20-22%), nitrogen (remainder), Argon in single digit ppm range,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  <2ppm). The flow

of purge gas was measured from 100 to 300 mL/min in 50 mL/min increments, with the TGA furnace temperature increased 5°C/min from room temperature to 800°C and cooled to room temperature to measure the next purge rate. The water signal (m/e 18) is chosen as representative but signals from other water fragments, CO<sub>2</sub> fragments and Ar displayed similar behavior. It is noted that if nitrogen is used as the purge gas, this same behavior is observed for oxygen from the ambient air. It is observed the water signal at purge flow of 100mL/min is higher than at increased purge flow rates, even at room temperature, indicating the MS immediately begins drawing in ambient air. The purge flow needed to be increased to 300mL/min to provide enough gas within the TGA furnace such that the MS turbo pump did not draw in any ambient air to compensate for a decreasing supply of gas molecules within the furnace.

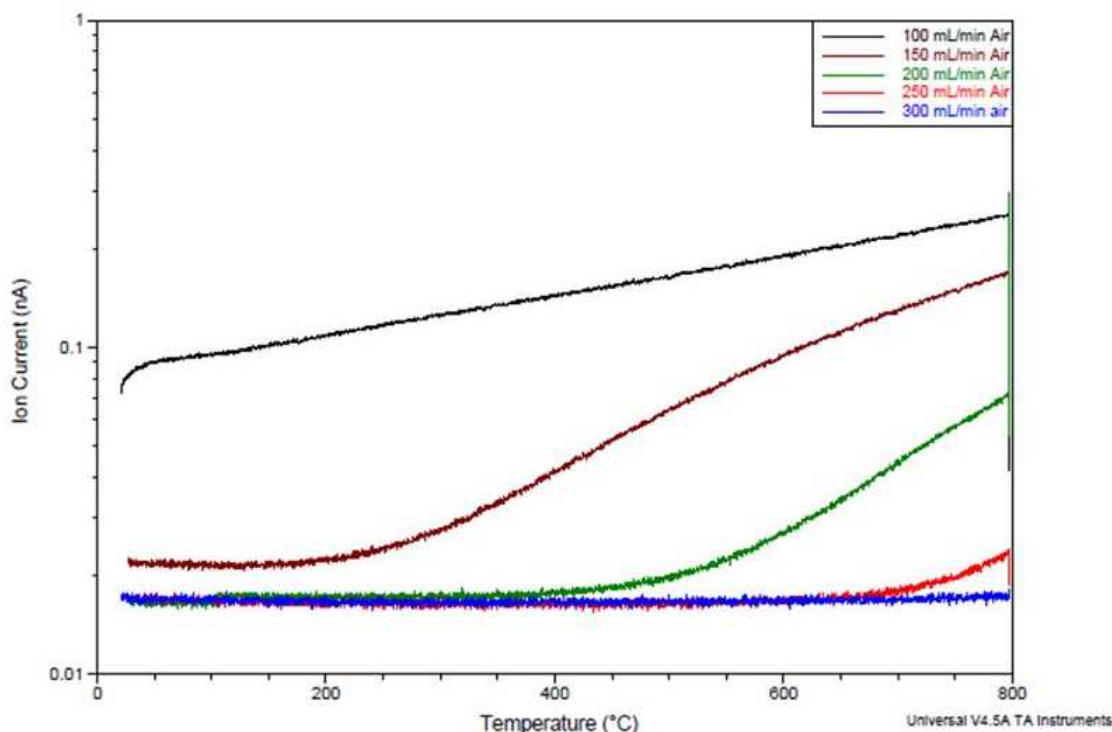


Figure A1. MS results for water using an empty sample pan using different purge gas flow rates. At 100mL/min, insufficient purge gas is introduced to the TGA furnace and ambient air is drawn into the MS capillary tube, as demonstrated by the much higher ion current. This amount is reduced as the flow is increased to 150mL/min. At 200mL/min, no ambient air is introduced at room temperature. Purge gas flow rate must be set to 300mL/min so that no ambient air is introduced at 800°C, the upper limit of the measurements in this report.

The purge gas flow rate was increased to 300 mL/min to ensure no water or CO<sub>2</sub> signals from ambient air were included in the MS results. However, the increased purge gas flow rate results in dilution of the gases generated from the sample. The turbo speed in the MS is not changing so

the increased amount of purge gas must exit the system via the TGA exhaust port. In so doing, the gases generated from the sample are, simply, diluted threefold (versus 100 mL/min purge gas flow). As the temperature of the furnace increases, increased amounts of purge gas exit, carrying more of the sample-generated gases out. It takes longer before the amount of iodine released can overcome this dilution effect and a portion of it gets drawn into the capillary.

Figure A2 displays the results from an older ORNL sample used to demonstrate this behavior: SNL label: KJC-2015-1-27-A, ORNL label: “11/4/13,” “Description: Iodine loaded reduced silver exchanged mordenite.” Results for two sample sizes are displayed (15.592mg and 32.380mg). For clarity, only water and iodine are included. It can be observed that the two TGA are very similar; the slight shift of the larger sample to the right would be due to the gases having a longer diffusion path through more material before they can exit the sample. It is also observed that a second decline in slope due to iodine loss begins at approximately 370°C for both samples, but iodine is not detected from the larger sample until ~450°C and from the smaller sample until ~480°C. In the current example, the iodine loss from the smaller sample was diluted by the purge gas enough so as to nearly escape detection. This behavior was also observed with the sample in the main body of this report.

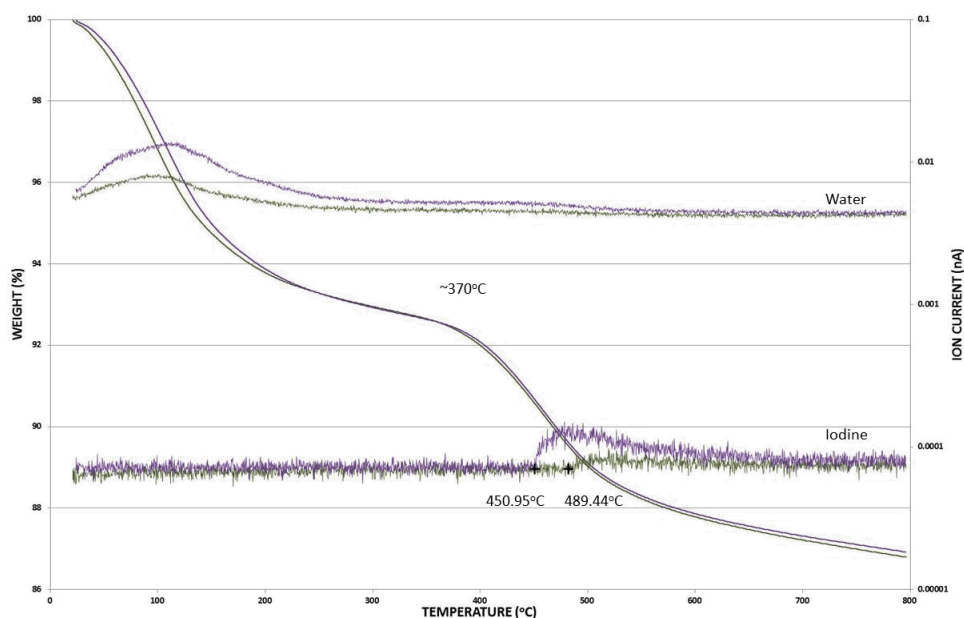


Figure A2. TGA and MS results for sample KJC-2015-1-27-A, two sample sizes. 300mL/min purge gas flow rate (air cylinder). Sample sizes 15.592mg and 32.380mg. The smaller sample results are green, the larger sample results are purple.



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